Study of adhesive and adhesion interface structure by spectroscopic analysis

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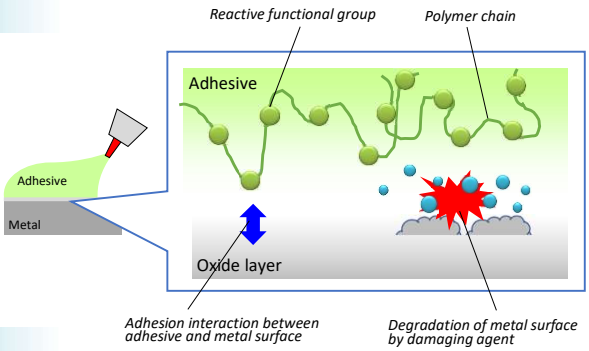
Background

✓Adhesion performance and its durability are strongly affected by physical or chemical structure between adhesive and adherent.

✓It is important to understand chemical structure of adhesive-adherent interface, which decide adhesion performance.

✓However, it is challenging to study adhesive and adhesion interface which have complicated and hetrogenious chemical structure and composition.

✓This study present a several analytical result of aluminium and epoxy–based adhesive interface by spectroscopic methods.



Analytical Methods and Results

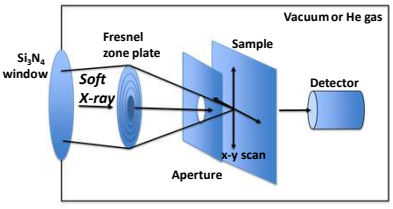
Materials
✓6000-type aluminium alloy
✓1C-epoxy adhesive (hardener: DICY)

Surface preparation
✓Sample 1: Alkaline degreasing, acid pickling
✓Sample 2: Mirror-polish, acid pickling

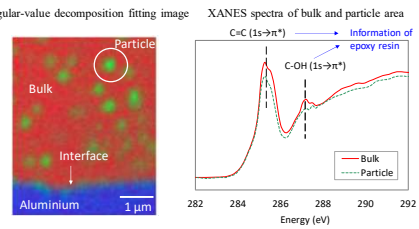
Adhesive application
✓Sample 1': Direct coat (100μm thickness) → For STXM
✓Sample 2': Dilute and spin coat (~20nm thickness) → For SFG and HAXPES

Scanning Transmission X-ray Microscopy; STXM

■Features
✓Using a Fresnel zone plate, soft X-rays are squeezed to a 50 nm square, and soft X-rays are scanned for transmitted X-ray measurement.
✓It can observe X-ray absorption spectra of target atoms with 50 nm square area.
➢Powerful tool to know a composition or chemical state of compounds contained in adhesive and metal surface in sub- to micrometer scale.



■Results
Sample 1'; size 10μm×10μm×100nm prepared by FIB

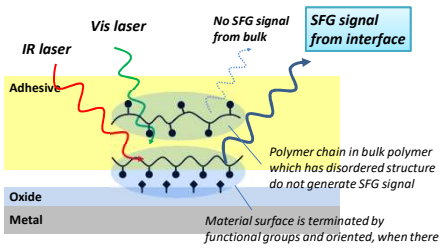


Two separated area was observed in adhesive which is epoxy resin-rich bulk and epoxy-less particle or interface.

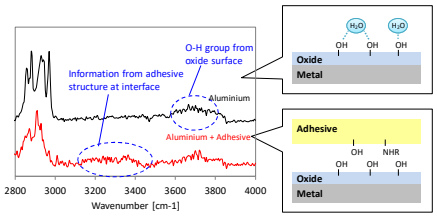
Q. Yuan, T. Itoh and Y. Takahashi, *PFNews*, 39, 2, 28 (2021).

Sum Generation Frequency Spectroscopy; SFG

■Features
✓Second non-liner optical phenomenon which is only active when the symmetry is broken.
✓Generate signal if a target material has oriented or asymmetric molecular structure
✓These structure are especially created between two material interface if they have chemical interaction
➢Unique method to estimate structure and chemical interaction at adhesion interface in molecular-level.



■Results
Sample 2 and 2'; Polarization, *ppp* (IR, UV, SFG)

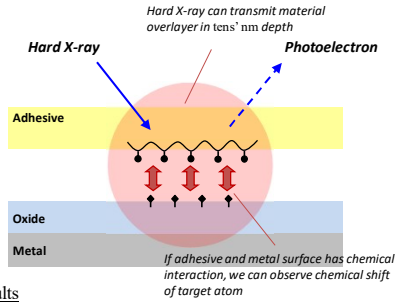


OH or NHR group may array in oriented structure at adhesive and alumunium interface and be engaged in adhesion.

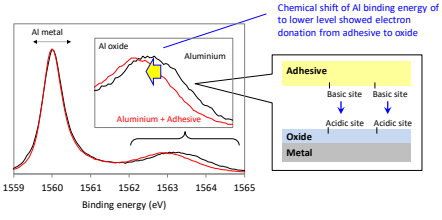
Y. Takahashi, S. Yamamoto, A. Kitahara, M. Yokomizo, K. Isoo, M. Sasaki, T. Miyamae, *J. Surf. Finish. Soc. Jap.* 72, 4, 238 (2021).

Hard X-ray Photoelectron Spectroscopy; HAXPES

■Features
✓Use of high energy and directive X-ray enable to analyze binding energy and chemical state of a target element in high resolution.
✓It can detect a photoelectron of target atoms at tens' nm of depth from surface
➢Non-destructive method to know a chemical state of metal surface and interaction with adhesive.



■Results
Sample 2 and 2'; X-ray energy 7947eV, Al 1s



Chemical shift may represent an electron donation from basic site of adhesive to acidic site of aluminiun oxide.

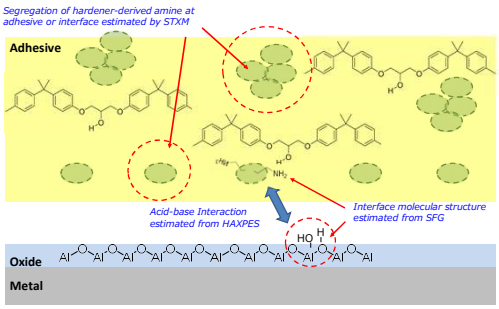
Summary and Acknowledgement

STXM : Epoxy resin-less particle or interface area exist which might be hardener rich

SFG : OH or NHR group array in oriented structure at adhesive and alumunium interface

HAXPES : Adhesive molecule donate electron to aluminium oxide

Proposed structure of epoxy adhesive and aluminium interface



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✓ SFG spectroscopy was performed by KOBELCO Research Institute, Inc and Prof. Dr. Takayuki Miyamae from Chiba university.
✓ HAXPES was performed by KOBELCO Research Institute, Inc at the BL16XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2018A5020, 2018B5020, 2019A5020).